

Interactive comment on “Explicit modelling of SOA formation from α -pinene photooxidation: sensitivity to vapour pressure estimation” by R. Valorso et al.

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Received and published: 28 June 2011

We thank the reviewers for their comments on the manuscript. We outline below responses to the points raised by each referee and summarise the changes made to the revised manuscript.

Reponses to Referee 1

1) Page 10131, lines 7-13: It is stated that some parameters were "set to achieve reasonable agreement between the simulated O₃, NO, and NO₂ concentrations and the observations, especially for the time profile of alpha-pinene removal".

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These parameters are stated to include the impact of chamber-specific wall removal of semi-volatile organics, but there actually appears to be no further information on this. Indeed, the “expected” insensitivity of the simulations of O₃, NO, NO₂ and alpha-pinene to vapour pressure estimation method and therefore the represented extent of the gas-aerosol partitioning of semi-volatile organics (stated on page 10132, lines 16-18) would suggest that the simulations of O₃, NO, NO₂ and alpha-pinene are probably also insensitive to including wall removal of semi-volatile organics, such that this process cannot be optimized on this basis. Ideally, this point should be clarified – particularly as the final paragraph of section 4.2 suggests that wall removal of product organics was actually not represented.

Chambers parameters such as wall uptake of semi-volatile compounds were indeed not optimised. The sentence about “deposition of semi-volatile compounds on the wall chamber” (p10131 lines 9-10) was misleading and will be removed.

2) Final paragraphs of sections 4.2 and 6: Some possible uncertainties and contributing factors to the systematic over-simulation of SOA are given. Perhaps the assumption of absorptive partitioning into an ideal liquid phase might be included here, given the results of some very recent studies (Virtanen et al., 2010; Vaden et al., 2011; Cappa and Wilson, 2011). Do the authors feel that the stated uncertainties collectively preclude absolute conclusions about the performances of the vapour pressure estimation methods?

These new insights on the gas/particle partitioning processes could indeed be a possible explanation for the divergences observed between the experiments and the modelled SOA. These recent results are of course expected to influence the theory of SOA formation. However, too little is currently known to have any comprehensive discussion on the relevance of our conclusions.

The following sentence will be added at the end of paragraph 4.2: “In addition, we simulated SOA formation assuming a gas/particle absorptive equilibrium into an ideal

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liquid phase. Recent papers suggest that the partitioning could occur according to an adsorptive/re-sublimation process between the gas and an amorphous solid phase (Virtanen et al., 2010; Vaden et al., 2011; Cappa and Wilson, 2011). These new insights could also be a possible explanation for the divergences observed between the experiments and the modelled SOA". The conclusions (sect. 6) will also be modified to include the following 4th point (P.10139, lines 17-18) " [...] (iv) the assumption of a gas/particle absorptive equilibrium into an ideal liquid phase instead of a gas/particle adsorptive/resublimation process into an amorphous solid phase".

3) The supplementary material shows that the mechanism generated in the present work performs similarly to the MCM scheme in relation to simulation of O₃, NO, NO₂ and alpha-pinene in the gas phase, at least for one experiment. Given that the MCM gas phase chemistry has previously been evaluated against data from other chambers (Saunders et al., 2003; Pinho et al., 2007), a brief mutually-supporting statement to this effect might be useful in main manuscript.

As suggested by the referee, the following sentence will be added p. 10132 line 10 in the revised version of the manuscript: "Simulations were also performed using the Master Chemical Mechanism (Saunders et al., 2003). Similar results are observed for the evolution of gaseous compounds (see Fig. S2). The disagreement in the simulated α -pinene decay seems therefore not specific to GECKO-A. The MCM has been evaluated against several chamber experiments for gas phase chemistry (Pinho et al., 2007) and the similar behaviour of both schemes provides a mutual support for an additional OH source in the high NO_x experiment."

Reponses to Referee 2

1 General comments

1.1 Extension the set of vapour pressure methods

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The authors have investigated the vapour pressure Myrdal-Yalkowsky (MY), combined with the Joback-Reid boiling point method, the Nannoolal vapour pressure method, combined with the Nannoolal boiling point method, and the SIMPOL method. Three methods is not that much for a sensitivity investigation. From the work of Barley (2010) and Compernelle (2010) one can see that MY combined with Joback-Reid gives relatively low vapour pressures, while the other two are intermediate. The authors should include at least one other method that gives rather high vapour pressures. The easiest way to do this is to include the MY method combined with the boiling point method of Nannoolal (2004), as they have already implemented these methods. This method also came out as second-best in the study of Barley (2010).

The objective of this work was to test the sensitivity of SOA formation to vapour pressure estimation methods which have been recommended or specifically designed for the purpose of SOA modelling. On the basis of the work of Camredon and Aumont (2006), Barley et al. (2010), Booth et al. (2010, 2011) and Pankow and Asher (2008), we selected to implement (1) the Myrdal and Yalkowsky combined with the Joback and Reid method, (2) the Nannoolal vapour pressure method combined with the Nannoolal boiling point method and (3) the SIMPOL method.

As requested by referee 2, we implemented the method combining Nannoolal boiling points with Myrdal and Yalkowsky vapour pressure (hereafter NAN/MY method). The results show that the simulated SOA concentration is largely underestimated in the low- and intermediate- NO_x experiment. In the high-NO_x experiment, no SOA is simulated using these vapour pressures. These results are consistent with those reported by Compernelle et al. (2010), showing that the use of NAN/MY underpredict aerosol amounts considerably. These outcomes reinforce the assumption that the systematic overprediction of the simulated SOA concentration might be due to an underprediction of the estimated vapour pressure with the 3 methods listed above. A sentence will be added to state this underestimation with NAN/MY (page 10133, line 29) and the results will be added in the Supplementary Material of the paper. However,

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the hypothesis of a systematic underestimation of the vapour pressure is not directly supported by the O:C analysis. The use of NAN/MY leads to higher simulated O:C ratios and is found to increase the discrepancies between model and observations. We will add a paragraph at the end of section 5.2 to discuss this outcome.

1.2 More thorough investigation of the reasons for the insensitivity to vapour pressure method.

On page 10133, line 21, the authors state: "Nevertheless, the simulated SOA concentrations show an unexpectedly low sensitivity to the method used to estimate P vap, well below the P^{vap} variability shown in Sect. 3 for the semi-volatile organic species." but they do not give an explanation. It could for example be that the different methods predict not very different vapour pressures for the top ten compounds. This is certainly possible, as the hydroperoxy compounds are important contributors to SOA, and the hydroperoxy group contribution is derived for all methods from the same, small set of vapour pressures. Agreement among the different methods would in this case certainly not imply a large reliability of the estimated vapour pressure for these compounds! This should be investigated. In case variability of predicted vapour pressure is indeed low among the top contributors, the authors should add a study with one or more methods with an added bias and/or random scatter to the estimated vapour pressures. This bias and scatter can be based on the results in Table 2. The authors compare the model results for one low, one intermediate and one high NOx experiment.

The vapour pressures of the top 10 species will be added in Table 4 and Table S1. The estimated vapour pressures for these major compounds differ from one to two orders of magnitude. The rather low sensitivity to P^{vap} is discussed below.

From Fig. 5 it is clear that, both experimentally and by modelling, the aerosol

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mass produced is the highest for experiment 1 and the smallest for experiment 3. It could be that ξ_i^{aer} is close to one for the important contributors for experiment 1, while it will be less for experiments 2 and 3, possibly closer to 0.5. Then the increasing variability to vapour pressure method in the order 1-2-3 would not be directly related to the high NOx conditions, but only to the lower aerosol mass. This should be investigated. This also means that for atmospheric simulations, where aerosol mass is low, sensitivity to vapour pressure estimation method will be much important than for smog chamber simulations with typically larger aerosol masses. This should be reflected in the discussion. Of course, the above considerations also apply to the aerosol composition. The ranking agreement is poorer for the simulations with higher NOx/lower SOA (Fig. S4), than for the low NOx/high SOA simulation (Fig. 7). This could be due to a ξ_i closer to 0.5. This should be reflected in the text. Also introducing a bias and random scatter (see above) could have a significant impact on the aerosol composition.

The following sentence will be added p.10133 at the end of the paragraph line 14: "The main contributors to the simulated SOA mass have vapour pressure between 10^{-9} and 10^{-11} atm (see Table 4, S1 and S2). As shown in Fig 1, such species will mostly be found in the aerosol phase ($\xi_i^{aer} > 0.9$) when the aerosol load exceeds $10 \mu\text{g m}^{-3}$ (as in the low- and intermediate-NOx experiment). The condensed fraction ξ_i^{aer} shows therefore a low sensitivity to P^{vap} values and thus P^{vap} estimates. For conditions where the aerosol concentrations are lower (as in the high-NOx experiment), a greater sensitivity of ξ_i^{aer} to P^{vap} values is observed (see Fig 5). For the high NOx experiment, the major contributors to SOA have ξ_i^{aer} around 0.5 to 0.9 (see Table S2). Note that for atmospheric conditions, sensitivity to vapour pressure is expected to be higher than shown for the smog chambers experiments simulated here due to lower background aerosol concentrations."

2 Specific comments

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p. 10124, line 15. The authors use 'MY' to refer to the Myrdal-Yalkowsky vapour pressure method, which is in their work combined with the Joback-Reid boiling point method. This gives the wrong impression that choice of boiling point method is only of secondary importance. It gives also the strange result that the 'MY' method gives the lowest vapour pressures and highest SOA yields, while it is stated in Barley (2010) that MY 'does have a bias towards overestimating vapour pressures'. Therefore I would recommend a naming that reflects the composite nature of the method, e.g. JR/MY.

The Myrdal and Yalkowsky vapour pressure method coupled with the Joback and Reid boiling point method will be named JR/MY in the revised manuscript and the Nannoolal vapour pressure method coupled with the Nannoolal boiling point method NAN/NAN.

p. 10127, line 14-16. This sentence is too vague. How are the criteria used to discriminate? Will at the end of the discrimination process only one isomer remain to represent all other isomers?

Is the order of the criteria, as tabulated in Table 1, relevant in this discrimination process?

The following sentences will be added in the revised version after the sentence lines 14-16: "For species having a production yield lower than 1×10^{-3} , [...]. The program scrolls down the list of the 20 criteria until one isomer remains. If more than one isomer remains at the end of the process, the one with the highest yield is kept as surrogate."

A figure demonstrating the lumping process (e.g. from 5 to 1 molecule) could help here. If the order of the criteria is relevant, have the authors investigated the impact of criteria ordering on the performance of the lumping process (accuracy of the lumped mechanism)?

p. 10127, line 18-21. On which systems was this tested? What is the size of the error induced by the lumping process?

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A detailed discussion of the lumping process used to reduce the size of the scheme is out of the scope of this article. The lumping process was necessary to reduce the chemical scheme down to a manageable size. However, the scheme remains nearly explicit: no simplification is performed for species having yields greater than 0.5 %, and the isomer substitution is highly constrained for species with yields greater than 0.1%. As a result, the scheme used here contains about 2×10^5 to 5×10^5 species (page 10128, line 18). The protocol implemented for the reduction and its evaluation will be described in more details in another article currently in preparation. Some additional information can be found in Aumont et al., Atmospheric Chemical Mechanism conference, Davis (California), 2008 (<http://airquality.ucdavis.edu/pages/events/2008/acm.html>).

p. 10127, line 24. Peeters and coworkers have provided important updates to the chemical oxidation mechanism of α -pinene by OH (Vereecken, 2007) since 2001, regarding the chemistry of one of the peroxy radicals. Why was this not used?

The chemical pathways provided by Peeters and coworkers are difficult to generalise and therefore to implement in the GECKO-A protocol. In addition, these proposed pathways involve the formation of a bicyclic peroxide alkyl radical, structure that can not easily be handled in the current version of GECKO-A. The chemical pathways provided by Peeters and coworkers were thus not considered in this study. We note however that these reactions are expected to lead to the formation of low volatile species. Taking these reactions into account would therefore likely increase the simulated SOA yield, which is already overestimated by GECKO-A. This update will likely not change the conclusion of the study.

p. 10128, line 1-5. According to quantum chemistry calculations, the described 1,7 H-shift is negligible compared to decomposition (Capouet, 2008). So why is this path used?

This 1,7 and 1,8 H-shift of α -carbonyl oxy radicals will be removed from the chemical

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scheme (and from Fig 3). Removing these reactions does not lead to significant changes in the results. This low sensitivity is due to the fact that these reactions are involved in the α -pinene + O₃ oxidation scheme, while for the conditions simulated here, OH radical is the main oxidant.

p. 10131, line 10-13. The authors state that photolysis constants and wall deposition of semi-volatiles were optimized parameters, and that the optimized parameters are given in Table 3. Yet I cannot find them there!

The J_{NO_2} and $J_{H_2O_2}$ corresponding to the optimized black lights intensity will be added in Table 3. Wall deposition of semi-volatile compounds is not accounted in the model (See answer to referee 1 above).

p. 10131. While the authors mention briefly the wall loss of gases, they do not mention wall loss of aerosol. Was it incorporated in the modelling study? Or was it already corrected for in the experimental data? This should be mentioned.

Experimental aerosol mass was wall loss corrected. The following sentence will be added (page 10131, line 5): "Experimental aerosol mass given below is wall loss corrected".

p. 10132, line 8. What could be the reason for the ozone overestimation? Mechanism uncertainty or a chamber artefact?

We performed simulations of the experiment with the MCM scheme (see the reply to referee 1, point 3) to check if the problem come specifically from the generated GECKO-A scheme. A similar ozone overestimation was found with the MCM. We performed some tests implementing typical Teflon chamber reactions as well. Chamber reactions were taken from Metzger et al. (2008). None of our tests could help to find an explanation for this ozone overestimation.

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Table 1. Crit. 9. Does 'conjugated carbonyls' only apply to ketones, as '-CO-CO-' seems to suggest? Then 'conjugated ketones' would be a better term, as aldehydes are also carbonyls.

This criteria 'conjugated carbonyls' concerns 'conjugated ketones' (R-CO-CO-R) as well as 'conjugated carbonyls at a terminal end of the chain' (criteria 17 to 20 namely -COCHO, -COC(O)OH, -COC(O)OOH, -COC(O)OONO₂ structures).

Crit. 13. What is exactly meant by 'conjugated carbonyls at a terminal end of the chain'? Does this also only apply to two ketone functionalities? A ketone cannot, by definition, be at the very end of a chain, then it would be an aldehyde. Are structures like -CO-CO-CH₃ meant? Note that also structures such as -C=C-C=O can be called 'conjugated carbonyls', which adds to the confusion.

See previous answer.

Crit. 5-8. Are nodes defined in the graph obtained from the hydrogen-suppressed molecule? This should be specified. Surprisingly, there is nothing on double bonds in this set of criteria, while the double bond is definitely important in mechanism construction. Was this investigated (e.g. conjugated double bonds vs. nonconjugated double bond, -C=C-C=O vs. nonconjugated alkenoic carbonyls).

Nodes refer to the carbon skeleton. Primary, secondary, tertiary and quaternary nodes are carbon atoms bound to 1, 2, 3 or 4 other carbons atoms of the skeleton, respectively. For example, a primary node might be a methyl group (-CH₃) or any functionalised carbon atom ending the carbon chain (e.g. -CHO, -CH₂(OH), -CO(OH) ...). Additional information will be given Table 1 to define nodes. Substitution is not allowed for species bearing a C=C bond. This sentence will be added in the text (page 10127, line 9).

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Table 3. Does '-' mean zero? This should be specified. The simulated photolysis frequencies should be included in 'optimized parameters', as well as the wall-loss parameters.

The symbol '-' means that no initial concentration, NO_x offgassing or OH source was implemented in the model. The symbol '-' will be replaced by " " in the revised paper. As there are more than one hundred of photolysis frequencies in the model, we will not incorporate all of them in Table 3 (sources for cross section and quantum yield are given in Aumont et al., 2005). Here, we optimised the black light intensity to retrieve the apparent $J_{H_2O_2}$ for the experiment, as explained page 10131, line 16-21. The retrieved $J_{H_2O_2}$ and J_{NO_2} are given in the text p.10131 but will also be added in Table 3 of the revised version.

Table 4, and Table S1: add vapour pressures of the top 10 compounds, and their condensed fraction ξ_i .

The estimated vapour pressures and ξ_i^{aer} will be added in Table 4, S1 and S2 for the top 10 species.

3 Technical corrections

All technical corrections were taken into account in the revised manuscript.

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